CHEM1047 – Week 5 Lecture 2 – Differentials

☐ *Chapter 5 of Cockett and Doggett, "Maths for Chemists", Vol 1.*

☐ *Sections 4.12 and 9.5 of Steiner, "The Chemistry Maths Book", 2nd edition.*

1. Formal definition of the differential

The *differential* is a generalisation of the notion of small increment. In the discussion so far, we were working with finite increments (*e.g.* Δf and Δx) or with limit expressions in which those increments vanished after the limit was taken. Differential expressions combine those methods: dx stands for an increment of x that is infinitesimally small. This eliminates the need for the correction terms that we previously had to use:

$$\begin{gathered} f(x+\Delta x) = f(x) + f'(x)\Delta x - \varphi(x,\Delta x)\Delta x \\ \Downarrow \\ f(x+\Delta x) - f(x) = f'(x)\Delta x - \varphi(x,\Delta x)\Delta x \\ \Downarrow \\ \Delta f = f'(x)\Delta x - \varphi(x,\Delta x)\Delta x \\ \Downarrow \\ df = f'(x)dx \end{gathered} \tag{1}$$

Differential expressions are smaller and more convenient than the expressions involving limits of finite increments. Equation (1) also clarifies the origin of *Leibniz's notation* for the derivative:

$$df = f'(x)dx \quad \Rightarrow \quad \frac{df}{dx} = f'(x) \tag{2}$$

2. Properties of differentials

The properties follow from the corresponding derivative properties. For sums and multiples:

$$d[f+g] = df + dg, \qquad d[\alpha f] = \alpha df \tag{3}$$

where α is a constant. For products and fractions:

$$d[fg] = fdg + gdf, \qquad d\left[\frac{f}{g}\right] = \frac{fdg - gdf}{g^2} \tag{4}$$

Here, d is not a variable or a function, but a *differential operator* – an instruction to compute the differential of whatever appears in front. The chain rule can now be derived in just one line:

$$df = f'(g)dg, \quad dg = g'(x)dx \quad \Rightarrow \quad d\left[f(g(x))\right] = f'(g(x))g'(x)dx \tag{5}$$

Deriving the rule for differentiating inverse functions is also now easy:

$$\begin{aligned} y = f(x) \quad &\Rightarrow \quad \frac{dy}{dx} = f'(x) \\ x = f^{-1}(y) \quad &\Rightarrow \quad \frac{dx}{dy} = \left(\frac{dy}{dx}\right)^{-1} = \frac{1}{f'(x)} = \frac{1}{f'\left(f^{-1}(y)\right)} \end{aligned} \tag{6}$$

The simplicity of such transformations is the reason why differentials are widely used. From the practical perspective, the differential is a local linear approximation to the function.

Example 1: calculate the differential of $\exp\left(-x^2/2\right)$.

Solution: from the definition in Equation (2)

$$d\left[\exp\left(-x^2/2\right)\right]=\exp\left(-x^2/2\right)d\left(-x^2/2\right)=-x\exp\left(-x^2/2\right)dx$$

Example 2: if $df/dx=\cos x$ and $x=t^3$, derive the expression for df/dt.

Solution: we can calculate dx and replace it

$$dx=3t^2dt \quad\Rightarrow\quad \frac{df}{dx}=\frac{df}{3t^2dt}=\cos\left(t^3\right) \quad\Rightarrow\quad \frac{df}{dt}=3t^2\cos\left(t^3\right)$$

Example 3: given that $y=a\sin\left(x\right)$, calculate dx/dy.

Solution: we can use the fact that dx/dy can be interpreted as a ratio of the two differentials

$$y=a\sin\left(x\right) \quad\Rightarrow\quad \frac{dy}{dx}=a\cos\left(x\right) \quad\Rightarrow\quad \frac{dx}{dy}=\frac{1}{a\cos\left(x\right)}$$

$$\frac{dx}{dy}=\frac{1}{a\sqrt{1-\sin^2\left(x\right)}}=\frac{1}{a\sqrt{1-y^2/a^2}}=\frac{1}{\sqrt{a^2-y^2}}$$

3. Differentials of multivariate functions

Multivariate functions change value if any of their arguments changes. The expression for the differential of a multivariate function therefore is:

$$df\left(x,y,z,...\right)=\frac{\partial f}{\partial x}dx+\frac{\partial f}{\partial y}dy+\frac{\partial f}{\partial z}dz+... \tag{7}$$

A subtle point here is that not every expression of the form

$$\left[...\right]dx+\left[...\right]dy+\left[...\right]dz+... \tag{8}$$

is a differential of a well-behaved function because mixed second derivatives must be equal, *e.g.*:

$$\frac{\partial^2 f}{\partial x\partial y}=\frac{\partial^2 f}{\partial y\partial x} \tag{9}$$

A differential that satisfies this property is called an *exact differential*. Such differentials are important in thermodynamics because their integrals are path-independent. To find out if a particular expression is an exact differential, one must compare mixed second derivatives, for example:

$$g\left(x,y\right)dx+h\left(x,y\right)dy \qquad \begin{array}{ll} \dfrac{\partial g}{\partial y}=\dfrac{\partial h}{\partial x} & \text{exact differential} \\[2ex] \dfrac{\partial g}{\partial y}\neq\dfrac{\partial h}{\partial x} & \text{not an exact differential} \end{array} \tag{10}$$

Here, $g\left(x,y\right)$ and $h\left(x,y\right)$ are already first partial derivatives of something – see Equation (7) – and therefore only one further derivative, with respect to the other variable, needs to be calculated.

Mixed derivative relations are useful in thermodynamics. Consider the full differential of enthalpy:

$$H=U+PV \qquad dH=dU+PdV+VdP \tag{11}$$

From the second law of thermodynamics $dU = TdS - PdV$, and therefore

$$dH = TdS + VdP \tag{12}$$

For this to be an exact differential, we must have:

$$\frac{\partial T(P,S)}{\partial P} = \frac{\partial V(P,S)}{\partial S} \tag{13}$$

Such relations are called *Maxwell's relations*.

Example 4: calculate the differential of $f(x,y) = x\sin y$.

Solution: from the definition

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = \frac{\partial}{\partial x}(x\sin y)dx + \frac{\partial}{\partial y}(x\sin y)dy =$$
$$= \sin(y)dx + x\cos(y)dy$$

Example 5: find out if $(x^2 - y^2)dx + 2xydy$ is an exact differential.

Solution: calculating mixed derivatives yields

$$\frac{\partial}{\partial y}(x^2 - y^2) = -2y \qquad \frac{\partial}{\partial x}(2xy) = 2y$$

The derivatives are not equal, and therefore the differential is not exact.